

Oxidation of Olefins with Potassium Permanganate in Oil/Water Emulsion¹

#1220

JOSEPH E. COLEMAN and DANIEL SWERN, Eastern Regional Research Laboratory,² Philadelphia, Pennsylvania

THE MILD OXIDATION of olefins with potassium permanganate in aqueous alkaline and neutral media has been studied in considerable detail (1, 3, 4, 6, 8, 10, 13, 14). The marked effect of pH on the type and yields of products formed from oleic acid under these conditions was recently demonstrated by us (1). It was confirmed that high-melting 9,10-dihydroxystearic acid is the major product of permanganate oxidation of potassium oleate in aqueous alkaline medium (pH 11-12), but by controlling the pH of the reaction in the neutral range (pH 9.0-9.5), the formation of 9(10),10(9)-ketohydroxystearic acids is favored.

Despite these detailed studies there remain many important aspects of this reaction yet unexplained. For example, the effects of low pH levels (acidic media) on the type of products formed has received little or no attention. The effect of permanganate to olefin ratios during the reaction is another neglected aspect. And still another is the effect of excess permanganate at various pH levels. It is toward these goals that the present investigation is directed.

Except for the work of Khan and Newman (5), in which stearolic acid was cleaved with potassium permanganate in an acidic dioxane solution, no information could be found on the permanganate oxidation of water-insoluble olefins, especially unsaturated fatty acids, in dilute acidic aqueous medium. Work in acidic medium has been neglected because a) it is not feasible to carry out oxidation of soaps of unsaturated fatty acids at low pH's, and b) olefins are insoluble in dilute aqueous solutions at acid concentrations below which the acid will react with the olefins by double bond addition.

Although it has been suggested that permanganate concentrations play a part in determining the type of products formed (14), this has not been adequately demonstrated, and the explicit effects of the permanganate content of an oxidation system and of pH have not been resolved. In this investigation it will be shown that when olefin content exceeds permanganate content during an oxidation, pH is the most important factor in determining the mode of reaction and the type of products formed. When permanganate content exceeds olefin content, the effects of pH are somewhat reduced. This investigation will also demonstrate the marked effects of large excesses of permanganate at various pH levels.

Since the oxidizing power of permanganate is greatest in aqueous acidic solution (11), the assumption was made that when the content of olefin exceeded that of permanganate in the system, more highly oxidized products should be obtained in aqueous acidic media than in neutral media; and in turn the products from the neutral media should be more highly oxidized than those formed in the alkaline media. That this line of reasoning is correct is readily seen upon comparing the known major product of oxidation in alkaline media (1,2-glycol) with that of neutral media (ketols). It will be shown that α -diketone is a main intermediate under similar mildly acidic conditions (pH 6-7) and cleavage predominates at low pH's (1-2).

To be able to handle water-insoluble olefins and thus have a general and uniform method of oxidation, emulsions of the oil/water type were employed. These were prepared with a nonionic emulsifier. The emulsions obtained were stable both to pH changes and to aqueous potassium permanganate solution.

To find out to what extent, if any, emulsions would alter or affect the reaction, several oxidations of emulsified oleic acid were conducted in alkaline and neutral media to compare the results obtained with those on soap solutions. The method of addition, time of reaction, and concentrations of oleic acid were the same as those published for soap solutions. High melting 9,10-dihydroxystearic acid and 9(10),10(9)-ketohydroxystearic acids were formed, respectively, in yields comparable to those obtained when homogeneous solutions of potassium oleate were used.

Two methods of oxidation were employed. The first method consisted of adding aqueous potassium permanganate solution to the emulsions at various pH levels, at such a rate that the content of olefin in the system always exceeded the content of permanganate. This method yielded predominantly intermediate (noncleavage) products when the stoichiometric quantities of permanganate were used. The second method consisted of adding the emulsions to the aqueous potassium permanganate solution at various pH levels, at such a rate that the content of permanganate always exceeded that of the olefin. This method yielded predominantly cleavage products. In these two methods the effects of pH on the type of products formed can be observed, both when the content of permanganate in the system is greater than olefin content and *vice versa*. These methods also demonstrated the marked effects of large excesses of permanganate upon the type of products formed from an

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² Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

olefin as well as the effects upon the intermediate products.

Experimental

Starting Materials. Purified oleic acid (iodine no. 89.0; oleic acid content 99%) was isolated from olive oil fatty acids as previously reported (7). Undecylenic acid (b.p. 136° at 1.5 mm. and n_D^{20} 1.4458); 1-octadecene (iodine number, 99.7); and cyclohexene were obtained by fractional distillation of the best commercial grades. The nonionic emulsifier used was Tween-20, a product of Atlas Powder Company. All other reagents were the purest available grades.

Oxidation of Emulsions. Method No. 1. Addition of Aqueous Potassium Permanganate Solution to Emulsions (Isolation of Intermediate Products). An emulsion was prepared by mixing 11.3 g. (0.040 mole) of oleic acid with 25 ml. of distilled water containing from 1–2% of nonionic emulsifier, based on oleic acid, and passing this mixture several times through a hand-operated laboratory homogenizer. The emulsion was placed in a 600-ml. beaker equipped with a stirrer, a thermometer, and electrodes attached to a continuous-reading pH meter. To the well-stirred emulsion an aqueous solution of potassium permanganate (approximately 20 ml. water/g.) was added dropwise at such a rate that the content of olefin in the system always exceeded that of permanganate. The quantity of potassium permanganate used depended upon the type of products desired, as will be described later under the specific oxidations. The pH was maintained at the desired level by the addition of 1 N sulfuric acid or sodium hydroxide as needed. The temperature was maintained between 5–10°C. by means of an ice bath. After the reaction was over (20 min. to 1 hr.), the reaction mixture was decolorized by the addition of an aqueous solution of sodium bisulfite, and 6 N hydrochloric acid was added until pH 1–2 was obtained. Usually the addition of hydrochloric acid broke the emulsion, but when this did not occur, the emulsion was broken by heating it on the steam bath to 60–70°C. The reaction mixture was then extracted with diethyl ether in a continuous extractor over-night (15 to 18 hrs.), and the ether was then evaporated from the crude reaction products. For product separation the crude reaction products were crystallized from various solvents.

Example No. 1. pH 12–13. To an oleic acid/water type of emulsion, 4.65 g. (0.0268 mole + 10% excess) of potassium permanganate in 80 ml. of distilled water were added dropwise with rapid stirring. The reaction was carried out at 5–10°C. and pH 12–13 and was discontinued after 20 min.; 9.8 g. of crude reaction products were recovered. Composition by analysis: 9,10-dihydroxystearic acid 78%; 9(10),10(9)-ketohydroxystearic acids 5%; unreacted oleic acid 12%; and unaccounted for 5%.

Example No. 2. pH 7–10. To an oleic acid/water type of emulsion 9.26 g. (0.0533 mole + 10% excess) of potassium permanganate in 200 ml. of distilled water were added dropwise with rapid stirring. The reaction was carried out at 5–10°C. and pH 7–10 and was discontinued after 30 min.; 11.7 g. of crude reaction products were recovered. Composition by analysis: 9,10-dihydroxystearic acid 17%; 9(10),10(9)-ketohydroxystearic acids 60%; 9,10-diketostearic acid 4% [determined polarographically (15)]; unreacted oleic acid 14%; and unaccounted for 5%.

Example No. 3. pH 6–7. To an oleic acid/water

type of emulsion, 13.9 g. (0.080 mole + 10% excess) of potassium permanganate in 250 ml. of distilled water were added dropwise with rapid stirring. The reaction was carried out at 5–10°C. and pH 6–7 and was discontinued after 30 min.; 12.3 g. of crude reaction products were recovered. The crude reaction products were washed with petroleum naphtha (hexane fraction), and the insoluble portion was filtered off. The insoluble solid weighed 7.0 g., and evaporation of the solvent from the filtrate yielded 5.3 g. of liquid. Composition by analysis of the insoluble solid: 9,10-dihydroxystearic acid 0%; 9(10),10(9)-ketohydroxystearic acids 30%; 9,10-diketostearic acid 25%; cleavage 28%; unreacted oleic acid 8%; and unaccounted for 9%. Composition by analysis of the liquid filtrate: cleavage 53%; unreacted oleic acid 33%; ketols 5%; and unaccounted for 9%.

Example No. 4. Large Excess of Permanganate. pH 6.5–7.5. To an oleic acid/water type of emulsion containing 14.1 g. (0.05 mole) of oleic acid in a 1000-ml. beaker, 34.7 g. (0.20 mole + 10% excess) of potassium permanganate in 700 ml. of distilled water were added dropwise with rapid stirring. The reaction was carried out at 20–30°C. and pH 6.5–7.5 and was discontinued after 30 min.; 14.5 g. of crude reaction products were recovered. The crude products were washed with petroleum naphtha, and the insoluble portion (8.0 g.) was filtered off. Evaporation of the solvent from the filtrate yielded 6.5 g. of residue. The insoluble portion was crystallized from absolute ethanol at 0°C.; 2.0 g. of 9,10-diketostearic acid (m.p. 83.5–85°C., % carbonyl oxygen 9.8) were obtained. Upon evaporating the solvent from this filtrate, 6 g. of azelaic acid (neutralization equivalent 100, m.p. 100–101°C.) were recovered. A mixed melting point with a sample of analytically pure azelaic acid gave no depression. From the residual unsaturation, neutralization equivalent, and typical pelargonic acid odor the first filtrate (6.5 g.) was judged to be a mixture of unreacted oleic acid (22%) and pelargonic acid (78%). The odor of shorter chain monobasic acids was absent. Since the liquid filtrate was not of interest, no further examination of it was made.

Example No. 5. Large Excess of Permanganate. pH 10–12. To an oleic acid/water type of emulsion containing 14.1 g. (0.05 mole) of oleic acid in a 1000-ml. beaker, 34.7 g. (0.20 mole + 10% excess) of potassium permanganate in 700 ml. of distilled water were added dropwise with rapid stirring. The reaction was carried out at 20–30°C. and pH 10–12 and was discontinued after 30 min.; 14.5 g. of crude reaction products were recovered. The crude products were crystallized from benzene at room temperature, and 5.8 g. of high-melting 9,10-dihydroxystearic acid (m.p. 129.5–131°C.; % hydroxyl oxygen 10.0) were filtered off. The benzene was evaporated from the filtrate, and the residue was crystallized from absolute ethanol at 0°; 2.7 g. of 9,10-diketostearic acid (m.p. 81.5–83°C.; % carbonyl oxygen 9.5) were obtained. The alcohol was evaporated from the second filtrate, and this residue was crystallized from petroleum naphtha at 0°C.; 3.0 g. of azelaic acid (neutralization equivalent 100; m.p. 100–101°C.) were separated. When the petroleum naphtha was evaporated from the filtrate, 3.0 g. of an oily liquid remained. The filtrate was moderately pure pelargonic acid (neutralization equivalent 165). The odor of shorter chain monobasic acids was absent.

Oxidation of Emulsions. Method No. 2. Addition of Emulsions to Aqueous Permanganate Solution (Cleavage). In a 1000-ml. beaker equipped with a stirrer, a thermometer, and electrodes attached to a continuous-reading pH meter an aqueous solution of potassium permanganate was placed. This solution was prepared by dissolving 34.7 g. (0.20 mole + 10% excess) of potassium permanganate in 700 ml. of distilled water (approximately 20 ml./g.) and adding 1 N sulfuric acid or sodium hydroxide to the desired pH level. Additional 1 N sulfuric acid or sodium hydroxide was added as needed during the oxidation to maintain the pH at the desired level. To this rapidly stirred aqueous solution of potassium permanganate, emulsions prepared as described in Method 1 were added. The temperature was maintained between 30–40°C. After the reaction was over (30 min. to 1 hr.), the reaction mixture was decolorized by the addition of an aqueous solution of sodium bisulfite, and 6 N hydrochloric acid was added to the higher pH level oxidations (pH 6.5–12) until pH 1–2 was obtained. This mixture was then heated on the steam bath to 60–70°C. to break the emulsion. The reaction mixture was extracted with diethyl ether in a continuous extractor over-night (15 to 18 hrs.) and handled as already described.

Example No. 1. Oleic Acid Cleavage. pH 10–12. An emulsion containing 14.1 g. (0.05 mole) of oleic acid was added with rapid stirring to an alkaline potassium permanganate solution (pH 12) prepared as described above. The reaction was carried out for 30 min. at a temperature between 30–40°C. and pH 10–12; 13.5 g. of crude reaction products were recovered. Crystallization from benzene at room temperature gave 1.45 g. of a precipitate which we were unable to identify. The benzene was evaporated from the filtrate, and the residue was crystallized from absolute alcohol at 0°C.; 2.8 g. of 9,10-diketostearic acid (m.p. 82.5–83°C.; % carbonyl oxygen 9.5) were obtained. When the ethanol was evaporated from the filtrate and the residue crystallized from petroleum naphtha at 0°C., 3.1 g. of crude azelaic acid (neutralization equivalent 104; m.p. 98–102°C.) were obtained. A mixed melting point of this compound with a sample of analytically pure azelaic acid gave no depression. The filtrate remaining after evaporation of the petroleum naphtha was a mixture of pelargonic acid and unidentifiable compounds. Detectable quantities of dihydroxystearic acid were conspicuously absent.

Example No. 2. Oleic Acid Cleavage. pH 6.5–7.5. In this experiment a smaller quantity of potassium permanganate was used. The purpose was to determine whether a smaller excess of permanganate would give cleavage or intermediate products at this pH. To an aqueous neutral solution of 17.4 g. (0.10 mole + 10% excess) of potassium permanganate in 375 ml. of distilled water, an emulsion containing 14.1 g. (0.05 mole) of oleic acid was added with rapid stirring. The reaction was carried out for 30 min. at a temperature between 30–40°C. and pH 6.5–7.5; 13.5 g. of crude reaction products were recovered. Crystallization from petroleum naphtha at 0°C. gave 6.5 g. of crude azelaic acid (neutralization equivalent 102; m.p. 99.5–102°C.). From the residual unsaturation, neutralization equivalent, and typical pelargonic acid odor the filtrate (7.0 g.) was judged to be a mixture of unreacted oleic acid (22%) and pelargonic acid (78%). It was not studied further.

Example No. 3. Oleic Acid Cleavage. pH 1–2. To the aqueous acidic solution of potassium permanganate, prepared as described originally in Method No. 2, an emulsion containing 14.1 g. (0.050 mole) of oleic acid was added with rapid stirring. The reaction was carried out for 1 hr. at a temperature between 30–40°C. and pH 1–2; 15.7 g. of crude reaction products were recovered. Crystallization from petroleum naphtha at 0°C. gave 9.2 g. of crude azelaic acid (neutralization equivalent, 102) and 6.5 g. of a light brown liquid by evaporation of the filtrate. Recrystallization of the precipitate from petroleum naphtha (5:1 ratio) at 0°C. gave 7.7 g. (82% yield) of azelaic acid as a white crystalline solid (neutralization equivalent, 99; m.p. 101–102°C.). No depression in melting point was noted when a mixed melting point was run with a sample of analytically pure azelaic acid. The neutralization equivalent of the filtrate was 172, and it possessed the typical odor of pelargonic acid. No further work was done on this fraction.

Example No. 4. Undecylenic Acid Cleavage. pH 1–2. An emulsion containing 9.3 g. (0.050 mole) of undecylenic acid was added with rapid stirring to an acidic potassium permanganate solution prepared as described originally in Method No. 2. The reaction was carried out for 30 min. at a temperature between 30–40°C. and pH 1–2; 9.8 g. of crude sebacic acid (neutralization equivalent, 116) were recovered. It was boiled with distilled water for 1 hr., and the small quantity of undissolved oil at the surface was discarded. The water solution was cooled to 5°C., yielding 6.7 g. (67%) of sebacic acid, m.p. 133°C., and neutralization equivalent, 102. No depression in melting point was noted when a mixed melting point was run with a sample of analytically pure sebacic acid.

Example No. 5. Cyclohexene Cleavage. pH 1–2. To an aqueous acidic solution of 23.1 g. (0.133 mole + 10% excess) of potassium permanganate in 450 ml. of distilled water, an emulsion containing 8.2 g. (0.1 mole) of cyclohexene was added with rapid stirring. The reaction was carried out for 30 min. at a temperature between 30–40°C. and pH 1–2; 8.5 g. of crude adipic acid (neutralization equivalent, 81) were obtained. Crystallization from 95% ethyl alcohol at 0°C. (5:1 ratio) yielded 7.5 g. (51%) of adipic acid (m.p. 151.5–152.5°C.; neutralization equivalent, 75). No depression in melting point was noted when a mixed melting point was run with a sample of analytically pure adipic acid.

Example No. 6. 1-Octadecene Cleavage. pH 1–2. An emulsion containing 12.6 g. (0.05 mole) of 1-octadecene was added with rapid stirring to an acidic potassium permanganate solution prepared as described originally in Method No. 2. The reaction was carried out for 1 hr. at a temperature between 30–40°C. and pH 1–2; 13.3 g. of crude reaction products (neutralization equivalent, 308), consisting largely of *n*-heptadecanoic acid, were recovered. Crystallization from acetone (10:1 ratio) at –10°C. yielded 12.5 g. of moderately pure *n*-heptadecanoic acid as a white precipitate (neutralization equivalent, 290; m.p. 58.5–59.5°C.). Four successive crystallizations of this product from 95% ethyl alcohol (5:1 ratio) yielded 7 g. (52%) of *n*-heptadecanoic acid, neutralization equivalent, 274. X-ray diffraction analysis indicated that the product was 99% *n*-heptadecanoic acid.

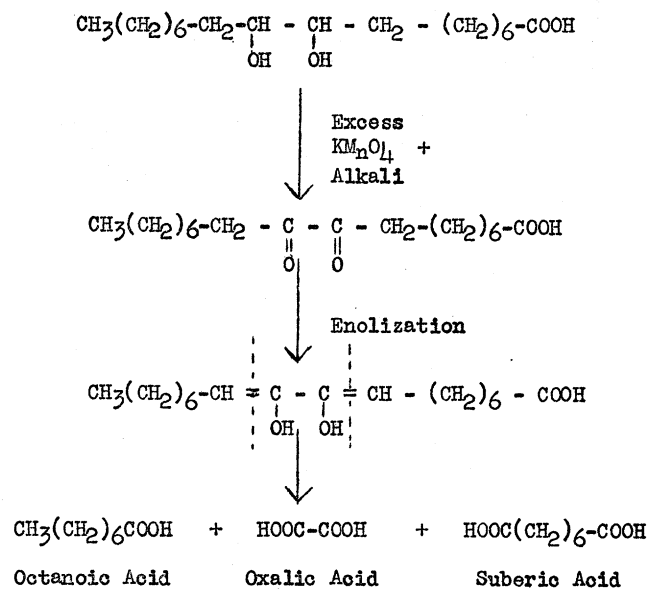
Results and Discussion

At pH 12–13, when olefin content during the reaction exceeds that of permanganate and stoichiometric quantities of the latter are used, high melting 9,10-dihydroxystearic acid accounts for approximately 90% of the oxidation products of emulsified oleic acid while 9(10),10(9)-ketohydroxystearic acids represent about 5%. Diketostearic acid is not detectable. When a similar oxidation is carried out at pH 7–10, 9,10-dihydroxystearic acid accounts for only 19% of the oxidized products whereas 9(10),10(9)-ketohydroxystearic acids account for about 70%. A small amount (4%) of diketostearic acid is also formed. At pH 6–7 no dihydroxystearic acid is formed, the conversion of oleic acid to 9(10),10(9)-ketohydroxystearic acids is reduced to 33%, but conversion to 9,10-diketostearic acid is increased to 27%. Cleavage products, arising presumably from 9,10-diketostearic acid, increase to 40%.

The following facts are clear concerning the potassium permanganate oxidation of oleic acid in emulsion when olefin content exceeds permanganate content and stoichiometric quantities of the latter are used: a) 9,10-dihydroxystearic acid is not a product in aqueous media at pH 6–7 but is the dominant product in alkaline media, pH 12–13; b) 9,10-diketostearic acid is not a product in aqueous alkaline media, pH 12–13, but is an important product in aqueous media, pH 6–7; and c) the formation of 9(10),10(9)-ketohydroxystearic acids is not favored in either strongly alkaline media, pH 12–13, or in aqueous media, pH 6–7. The type and yield of products formed are dependent both upon the oxidizing power of the permanganate and upon the pH.

It has been suggested that, under the above specified conditions, 9,10-dihydroxystearic acid and 9(10),10(9)-ketohydroxystearic acids are not intermediates in the formation of 9,10-diketostearic acid but that the last-named is presumably formed by oxidative attack on both carbon atoms of a common, unhydrolyzed complex (1, 14). Since 9,10-diketostearic acid is a product of oxidation in mildly acidic media (pH 6–7), attack on both carbon atoms of the complex must be favored under these conditions. This is in contrast to oxidation at pH 9 (ketol formation), where only one carbon atom of the complex is oxidatively attacked, and to oxidation in alkaline medium (pH 12) where neither carbon atom of the complex is oxidatively attacked but hydrolysis predominates. We wish to propose therefore that the initial reaction of permanganate with olefins at all pH ranges is the formation of a single complex, with the subsequent reactions depending on the pH when the permanganate is not in large excess.

When the content of permanganate in the system exceeds the content of oleic acid (oxidation by Method 2), the characteristic intermediate products just discussed are not obtained. In the acidic and neutral media, cleavage products are obtained in high yields, but the low pH oxidations (1–2) give more complete cleavage (80% yields) and less complex products. It is not clear however whether intermediate products are first formed and cleavage occurs thereafter or whether cleavage occurs on the carbon atoms while they are still a part of the complex. In the alkaline medium (Method 2) a variety of products are obtained from oleic acid. 9,10-Diketostearic acid, azelaic and pelargonic acids, and unidentified acidic com-



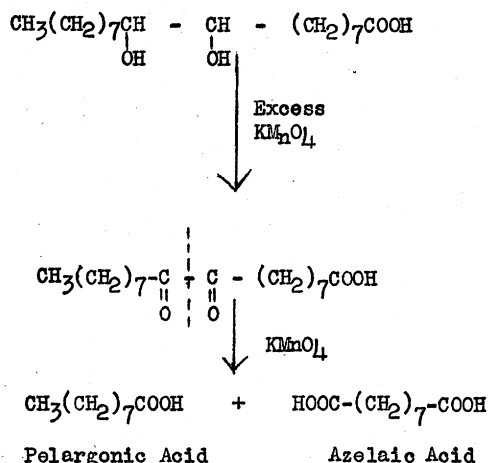
pounds are among the products. The difference in products obtained at various pH levels demonstrates that pH does affect the type of products formed, even when permanganate is in excess.

When large excesses of permanganate are used with oleic acid, even in Method 1, different products are obtained from those under the same pH conditions when stoichiometric quantities of permanganate for production of intermediate products are used. In the acidic and neutral media, cleavage products are dominant, but Method 2 is still preferred for cleavage because the composition of the oxidation products is simpler. Since the intermediate oxidation products of oleic acid at these pH levels are known when stoichiometric quantities of permanganate are used, the cleavage products obtained by Method 1 with excess permanganate are believed to be derived from the further oxidation of these intermediate products. In the alkaline medium however, numerous products are obtained with none predominating. A typical composition by analysis of the isolated reaction products from oleic acid oxidation is: 9,10-dihydroxystearic acid 40%; 9,10-diketostearic acid 20%; azelaic acid 18%; pelargonic acid 18%; and ketols 4%. It is believed that the 9,10-diketostearic acid and azelaic and pelargonic acids are derived from the further oxidation of 9,10-dihydroxystearic acid.

That azelaic and pelargonic acids are obtained from the further oxidation of 9,10-dihydroxystearic acid in alkaline medium may seem in conflict with the reports of Spiridonov (12), Lapworth (9), and Green (2). In these reports suberic, octanoic, and oxalic acids are the sole products of the permanganate oxidation of 9,10-dihydroxystearic acid in alkaline medium. These authors however used not only a large excess of potassium permanganate but also a large excess of alkali (approximately 16 moles per mole of 9,10-dihydroxystearic acid). It is believed that the initial step in such reactions is the oxidation of the hydroxyl groups to carbonyl groups, followed by enolization of the carbonyl groups, brought about by the excess alkali. Further oxidation of the enolized form would produce suberic, octanoic, and oxalic acids, as shown.

On the other hand, azelaic and pelargonic acids are obtained from the further oxidation of 9,10-di-

hydroxystearic acid (as in this investigation) when excess alkali is absent. Although the initial step is also presumed to be the oxidation of the hydroxyl groups to carbonyl groups, enolization cannot take place because of the absence of excess alkali. Further oxidation therefore occurs between the carbonyl groups of 9,10-diketostearic acid, and azelaic and pelargonic acids are the resulting products, as shown.



The intermediate oxidation products of cyclic and terminally unsaturated hydrocarbons, under conditions which gave essentially no cleavage with oleic acid (Method 1), were cleaved to a considerable extent even in alkaline and neutral media (results not detailed in this paper). Oxidation at pH 10–12 with the quantity of permanganate calculated to give glycol or ketol yielded only about 66% of mixtures of glycols and ketols and as much as 34% of acidic cleavage products.

From undecylenic acid by Method 2, sebacic acid was obtained in high yields, and adipic acid was obtained from cyclohexene in 50% yield. From 1-octadecene an 86% yield of crude and 52% yield of pure *n*-heptadecanoic acid was obtained. Aqueous acidic potassium permanganate oxidation therefore provides a method not only for preparing dibasic acids from terminally and nonterminally unsaturated fatty acids and cyclic hydrocarbons but also for preparing monobasic acids with an odd number of carbon atoms from readily available, terminally unsaturated hydrocarbons.

Summary

Oxidation of water-insoluble olefins, such as oleic and undecylenic acids, cyclohexene, and 1-octadecene, has been conducted in oil/water emulsions, using a nonionic emulsifier. Emulsions of these olefins were sufficiently stable over a wide pH range to permit rapid and efficient oxidations to be carried out from pH 1–12.

Two methods of oxidation were employed. Method 1 consisted of adding aqueous potassium permanganate solution to the emulsion at various pH levels, at such a rate that the content of olefin in the system always exceeded that of permanganate. Method 2 consisted of adding the emulsion to the aqueous po-

tassium permanganate solution at various pH levels, at such a rate that the content of permanganate in the system always exceeded that of olefin.

In Method 1, when stoichiometric quantities of permanganate were used, glycols and ketols were the main products from emulsified cyclohexene and 1-octadecene, under alkaline and neutral conditions, but substantial cleavage also occurred. Oleic acid in emulsion under similar conditions was also oxidized in the alkaline (pH 12) and neutral (pH 9) regions to form high-melting 9,10-dihydroxystearic acid and 9(10),10(9)-ketohydroxystearic acids, respectively, as the major products with essentially no cleavage. The yields were comparable to those obtained when potassium oleate was oxidized in dilute solution by previously published procedures. 9,10-Diketostearic acid was a major product of the mild aqueous acidic (pH 6–7) permanganate oxidation of oleic acid under the above specified conditions (Method 1).

In Method 2 dibasic acids were obtained in good yields from oleic acid, undecylenic acid, and cyclohexene at pH 1–2. An improved method for preparing monobasic acids with an odd number of carbon atoms from terminally unsaturated hydrocarbons with an even number of carbon atoms has also been reported.

When excess permanganate was used in either oxidation method, cleavage occurred at all pH levels but was more complete at low pH levels by Method 2. When excess permanganate was used in Method 1, the intermediate products from oleic acid were further oxidized. At low pH levels (1–7) these intermediates were converted almost exclusively to azelaic and pelargonic acids; at high pH levels (8–12) they were converted to a mixture of more highly oxidized products, including azelaic and pelargonic acids.

The oxidizing power of potassium permanganate increases with reduction in pH and, when olefin content exceeds permanganate content in the systems, pH is the most important factor in determining the mode of reaction and the type of oxidized products formed. When an excess of potassium permanganate is available, the effect of pH is not as dramatic.

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REFERENCES

1. Coleman, J. E., Ricciuti, C., and Swern, Daniel, *J. Am. Chem. Soc.*, **78**, 5342–5345 (1956).
2. Green, T. G., and Hilditch, T. P., *J. Chem. Soc.*, 764–767 (1937).
3. Hilditch, T. P., and Plimmer, H., *J. Chem. Soc.*, 204–206 (1942).
4. Holde, D., and Marcusson, J., *Ber.*, **36**, 2657–2662 (1903).
5. Khan, N. A., and Newman, M. S., *J. Org. Chem.*, **17**, 1063–1065 (1952).
6. King, G., *J. Chem. Soc.*, 1788–1792 (1936).
7. Knight, H. B., Jordan, E. F. Jr., Roe, E. T., and Swern, Daniel, "Biochemical Preparations," vol. II, pp. 100–104, John Wiley and Sons Inc., New York, N. Y. (1952).
8. Lapworth, A., and Mottram, E. N., *J. Chem. Soc.*, **127**, 1628–1632 (1925).
9. Lapworth, A., and Mottram, E. N., *J. Chem. Soc.*, **127**, 1987–1989 (1925).
10. Morrell, R. S., and Phillips, E. O., *J. Soc. Chem. Ind.*, **57**, 245–247 (1938).
11. Moeller, T., "Inorganic Chemistry," p. 884, John Wiley and Sons Inc., New York, N. Y. (1952).
12. Spirodonov, J. Russ. Phys. Chem. Soc., **19**, 646 (1887).
13. Wagner, G., J. Russ. Phys. Chem. Soc., **27**, 219 (1895).
14. Wiberg, K. B., and Saegbarth, K. A., *J. Am. Chem. Soc.*, **79**, 2822–2824 (1957).
15. Willits, C. O., Ricciuti, C., Knight, H. B., and Swern, Daniel, *Anal. Chem.*, **24**, 785–790 (1952).

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